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Improving the Hydrolytic Stability of Aryl Cyanate Esters by Examining the Effects of Extreme Environments on Polycyanurate Copolymers

Alasdair O. Crawford, Gabriel Cavalli, Brendan J. Howlin, and Ian Hamerton*

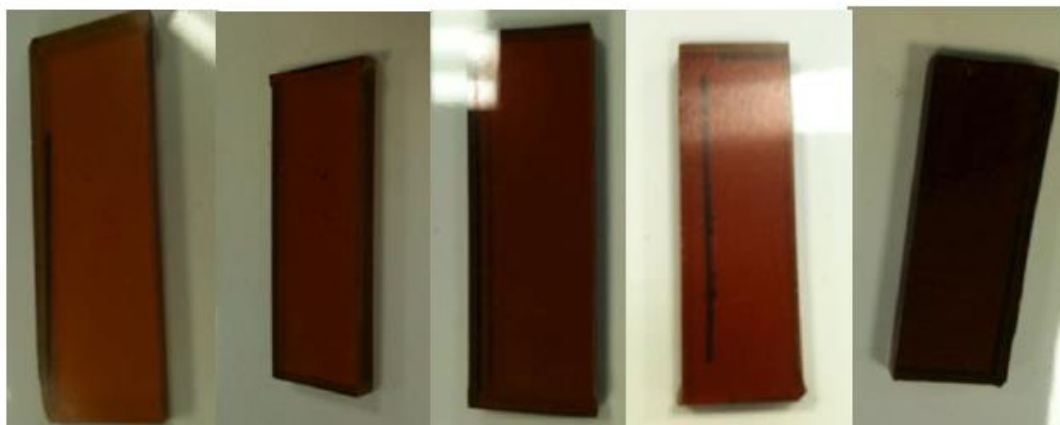


Fig. S1. Images of selected blends between 1-3.

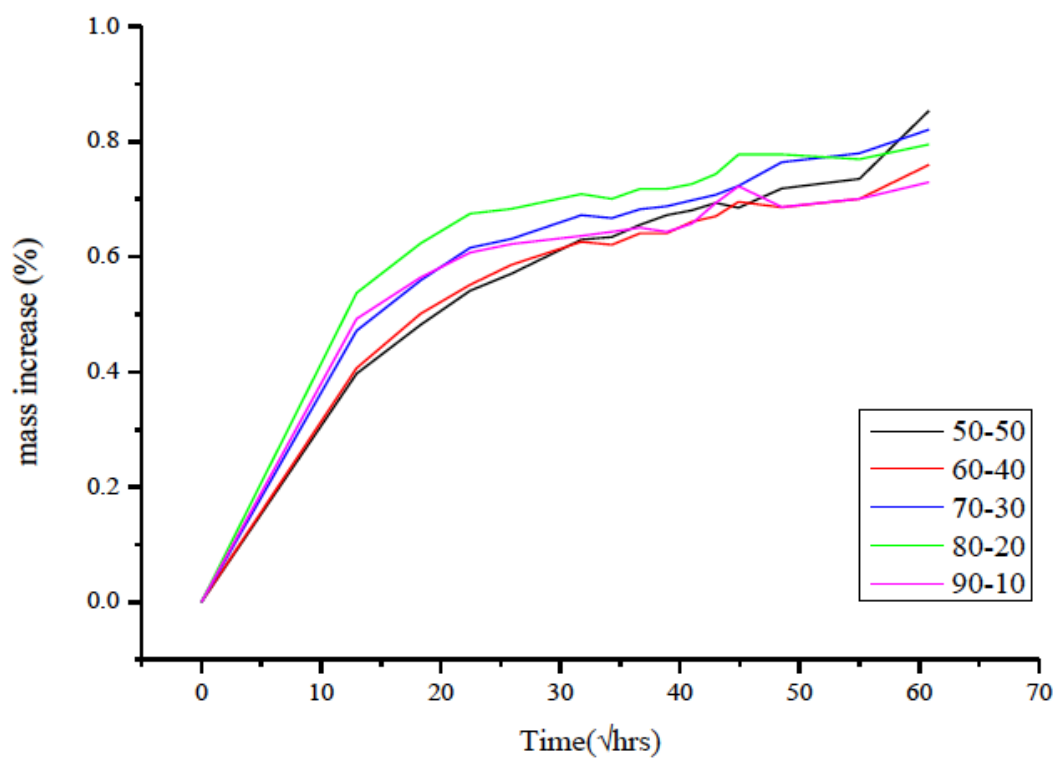


Fig. S2. $[I_x-2_y]$ H₂O absorbed (%) vs. time (√hrs) at 75 % RH

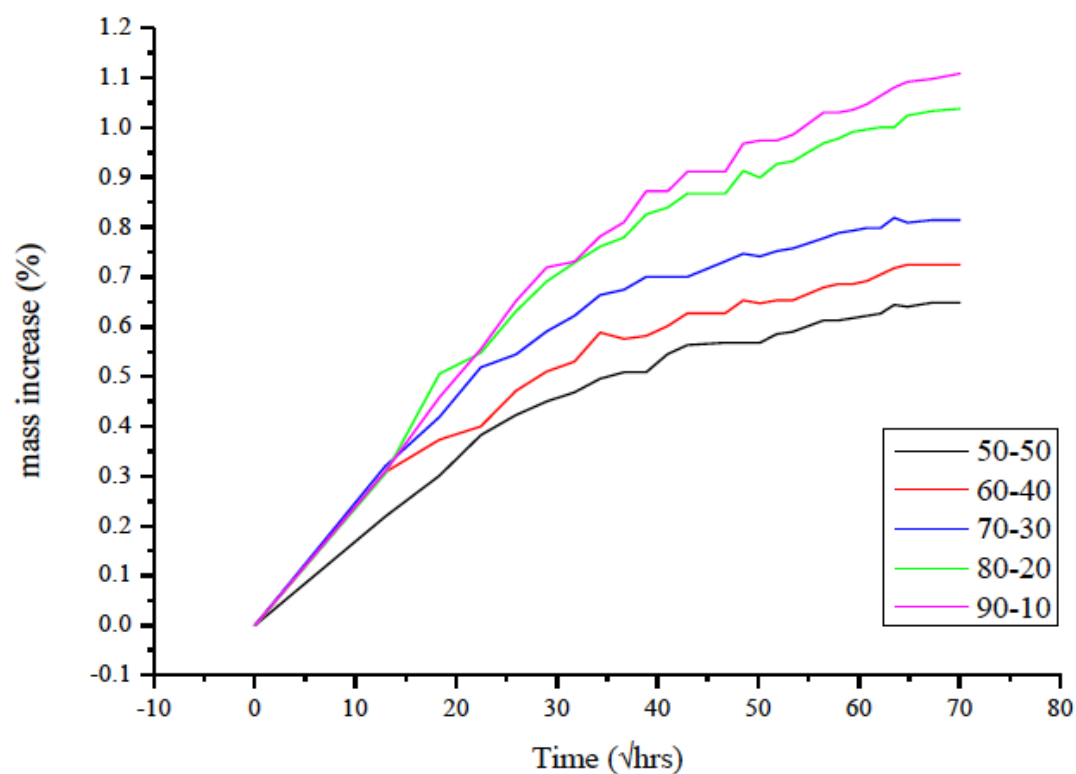


Fig. S3. $[3_x-1_y]$ H₂O absorbed (%) vs. time ($\sqrt{\text{hrs}}$) at 75 % RH

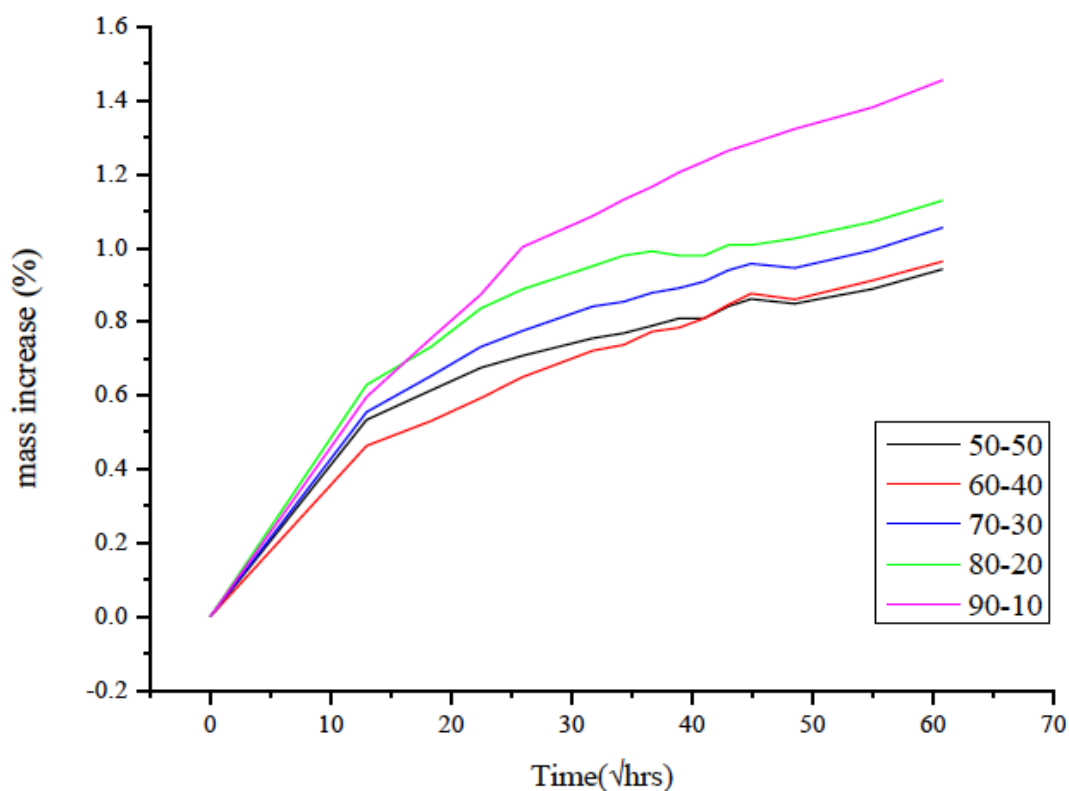


Fig. S4. $[3_x-2_y]$ H₂O absorbed (%) vs. time ($\sqrt{\text{hrs}}$) at 75 % RH

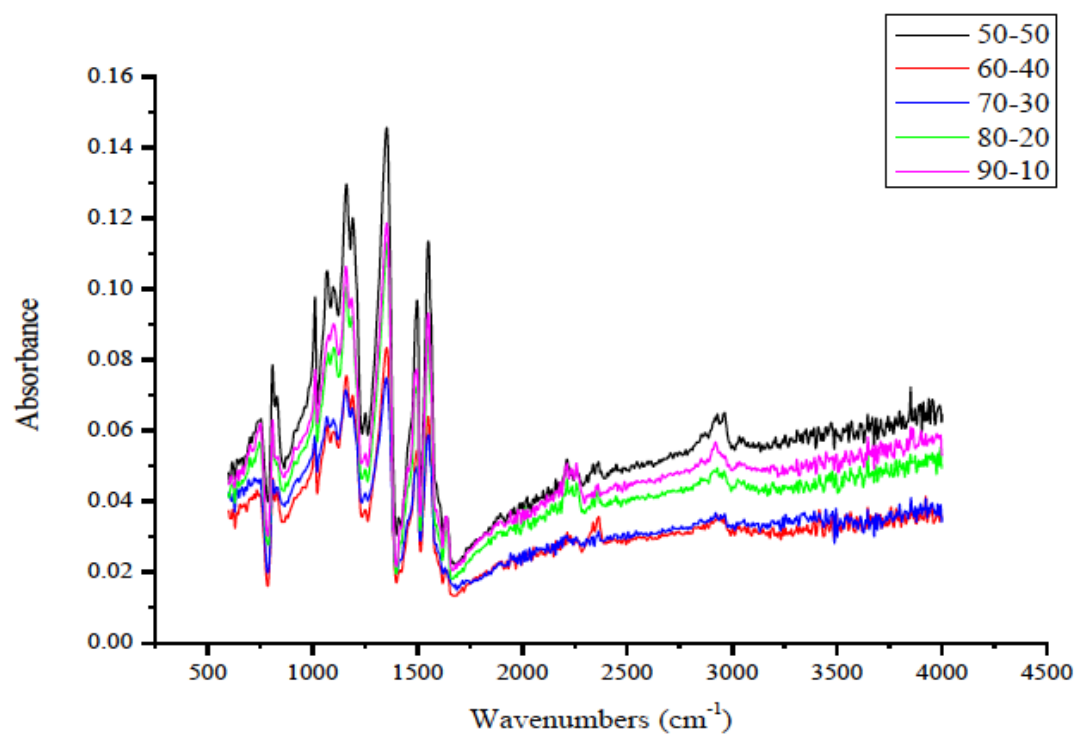


Fig. S5. Spectral analysis of $[3_x-1_y]$

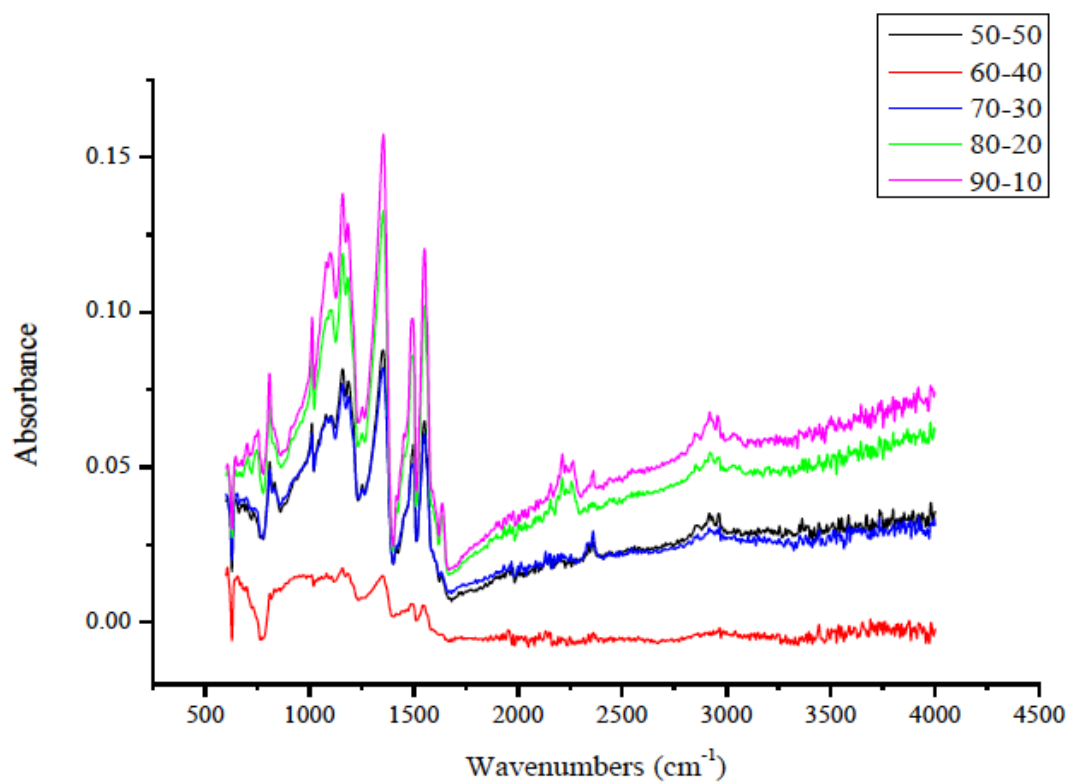


Fig. S6. Spectral analysis of $[3_x-2_y]$

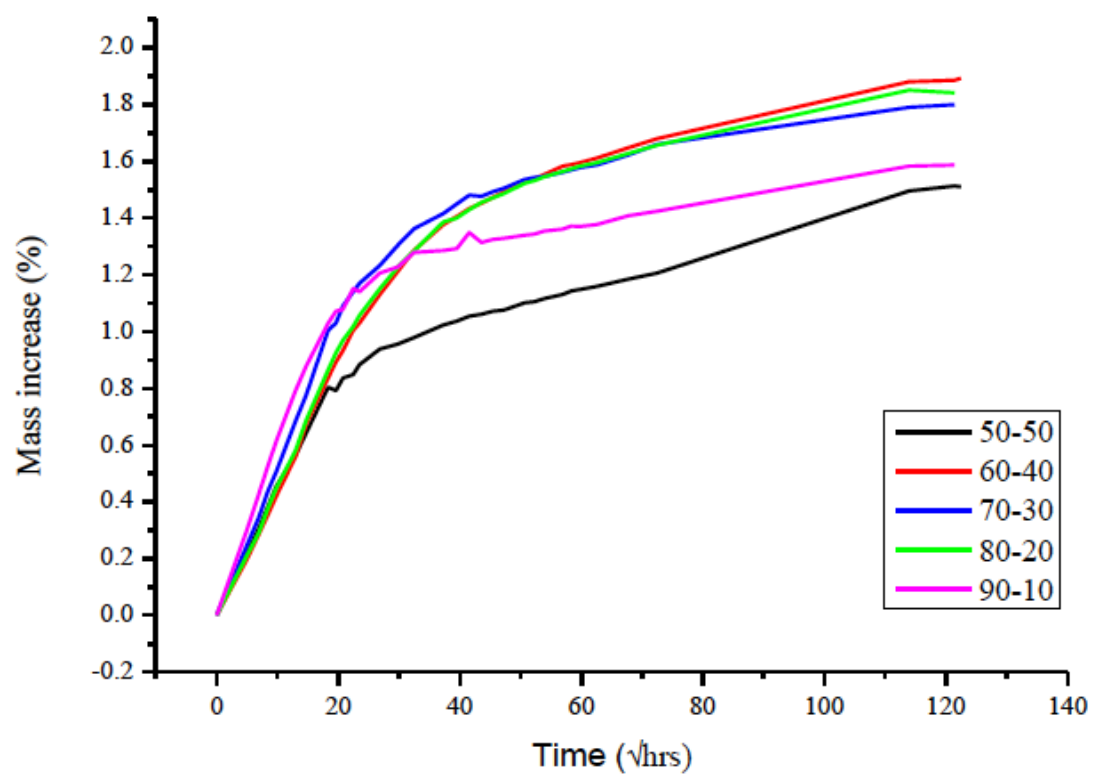


Fig. S7. $[I_{x-2y}]$ H₂O absorbed (%) vs. time ($\sqrt{\text{hrs}}$)

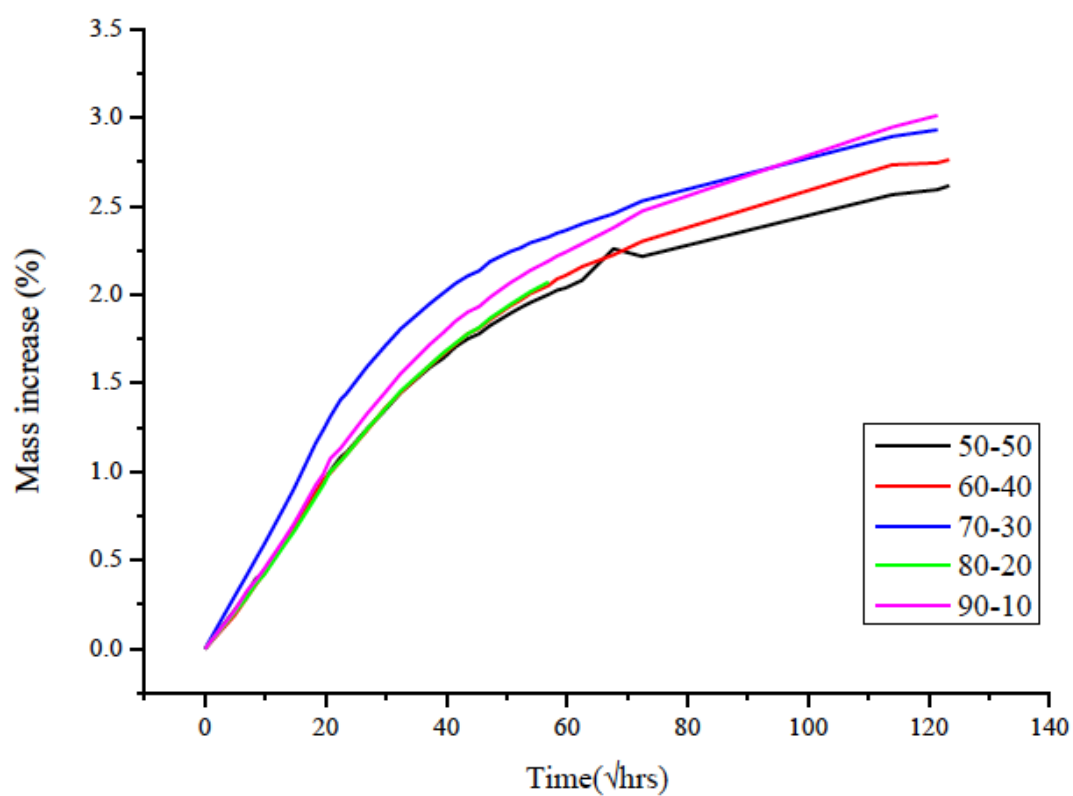


Fig. S8. $[3_x-1_y]$ H₂O absorbed (%) vs. time ($\sqrt{\text{hrs}}$)

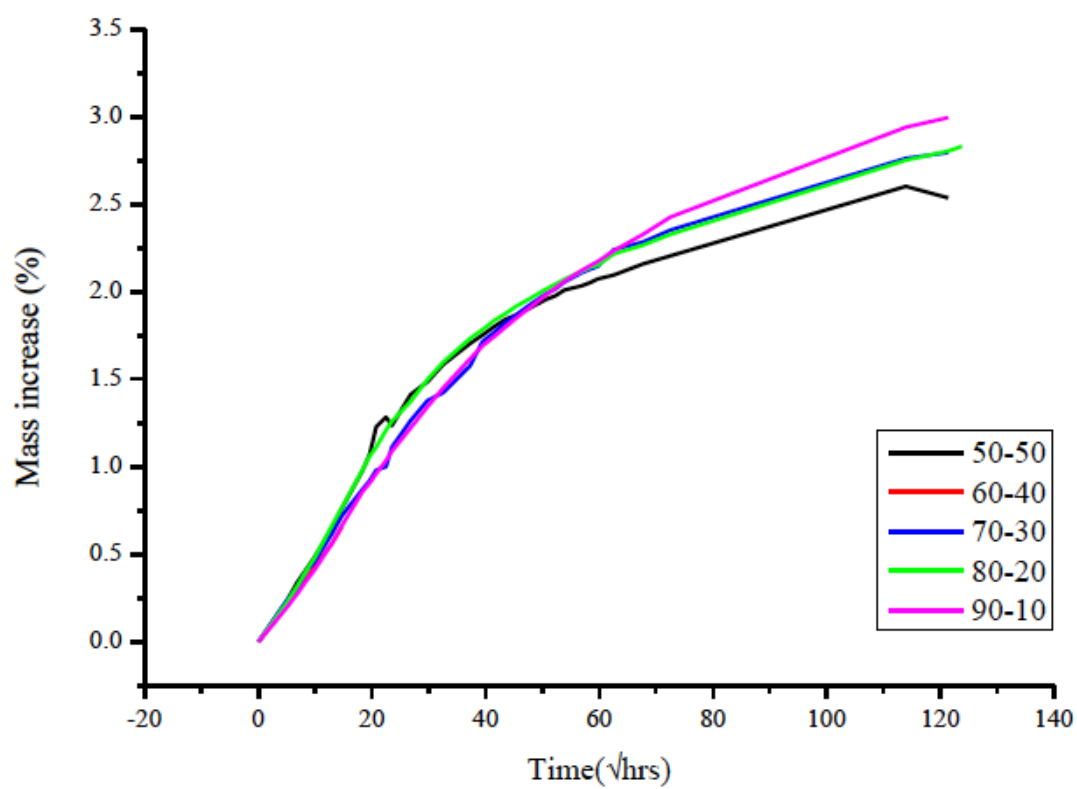


Fig. S9. $[3_x-2_y]$ H₂O absorbed (%) vs. time ($\sqrt{\text{hrs}}$)

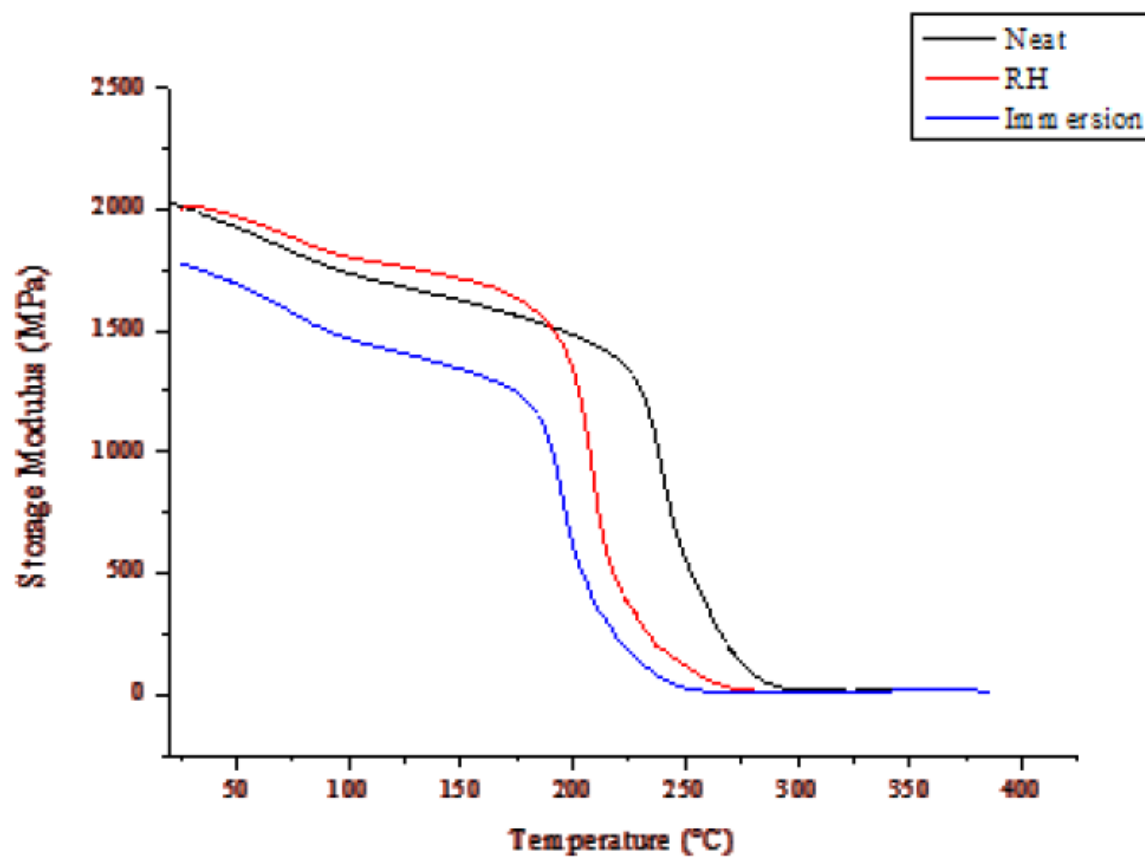


Fig. S10. DMTA data for unexposed (black), RH (red) and immersion (blue) for the blend [I₅₀-2₅₀] showing storage modulus as a function of temperature.

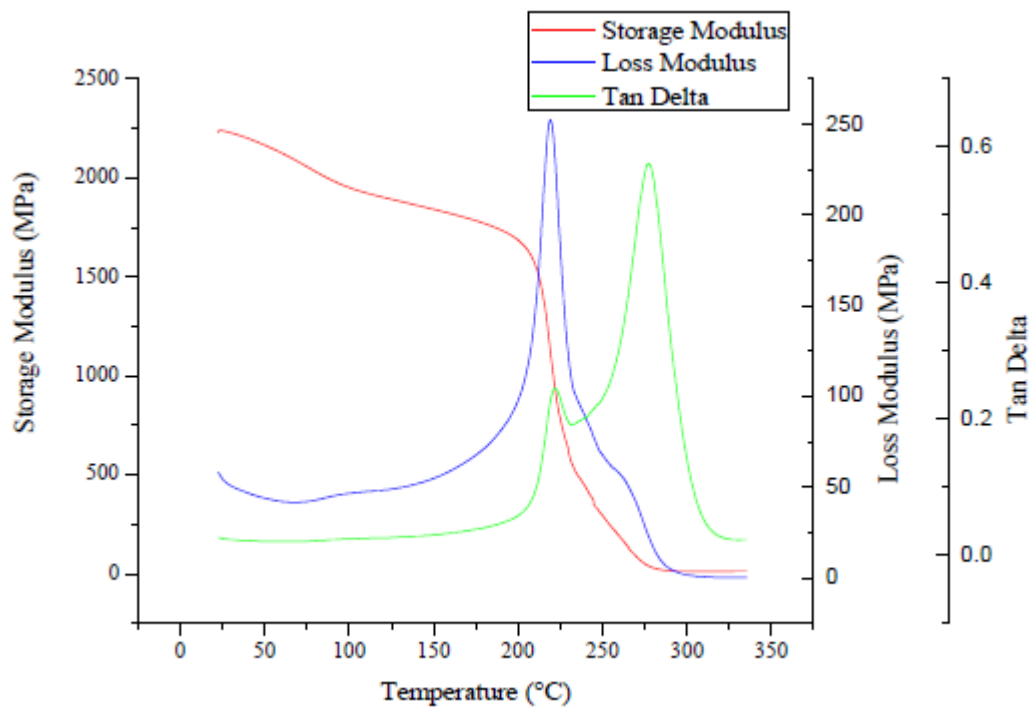
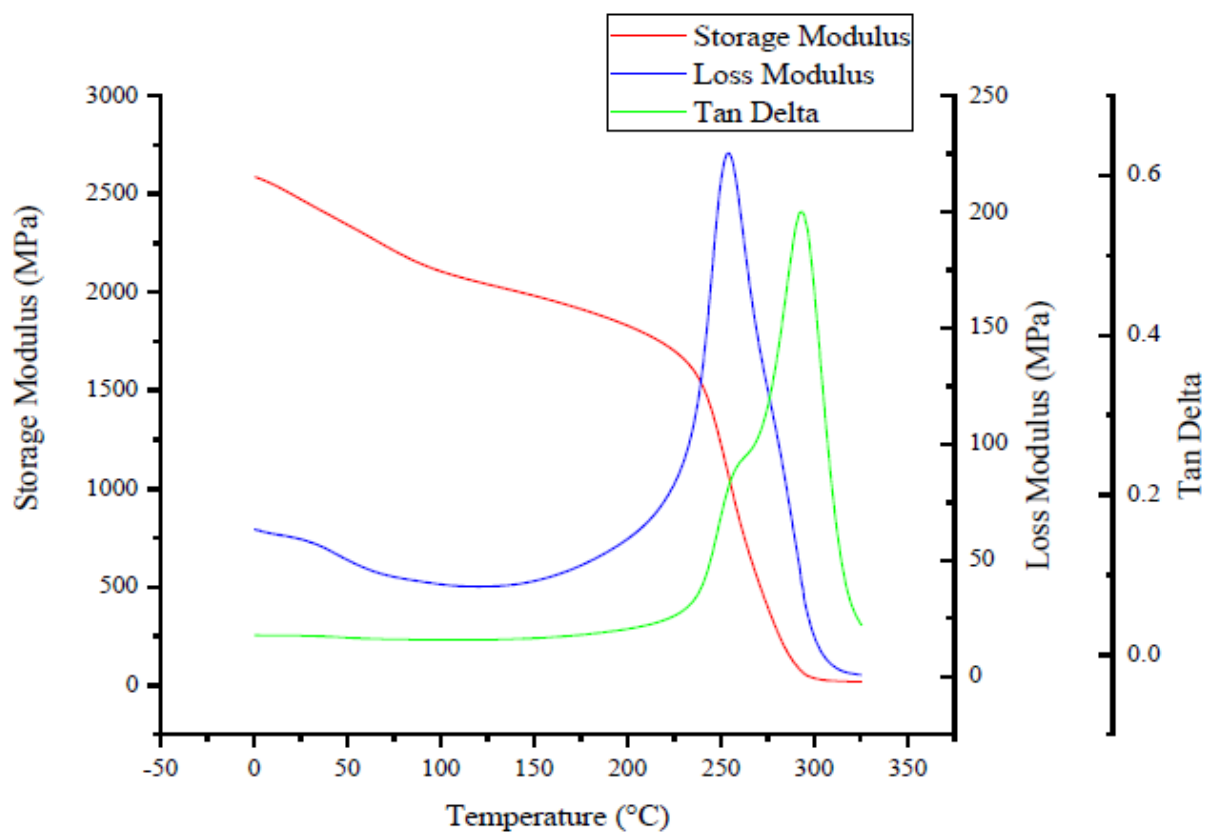


Fig. S11 DMTA data for I_{70-230} (top) and $[I_{70-230}]$ (bottom) showing storage and loss moduli as a function of temperature.

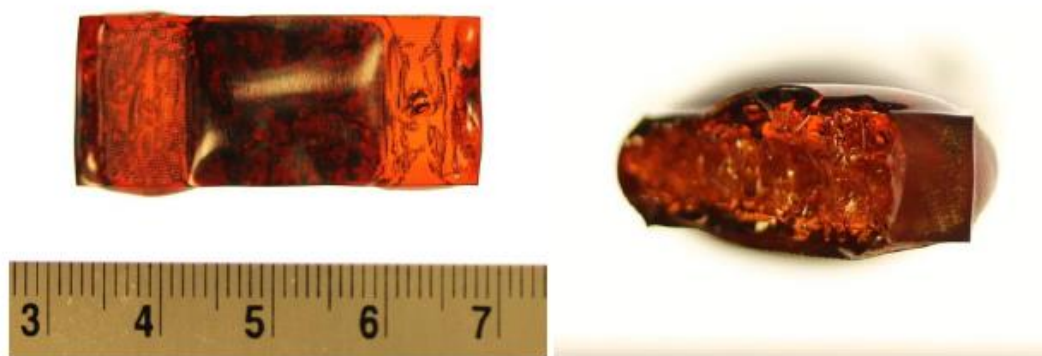


Fig. S12 High resolution images of outgassing in [(1)₅₀-(2)₅₀]

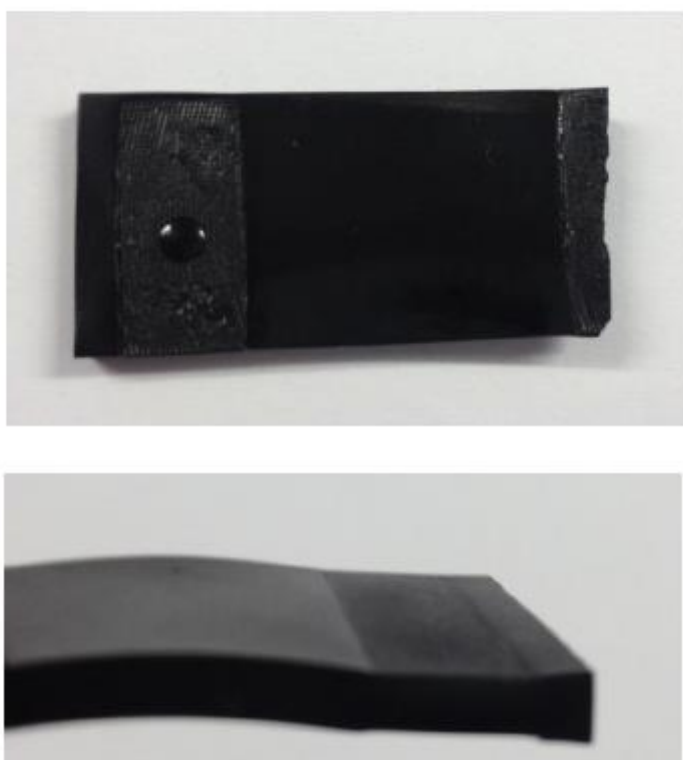


Fig. S13 Top view (above) and side view (below) of [(3)₉₀-(2)₁₀] following exposure and DMTA.

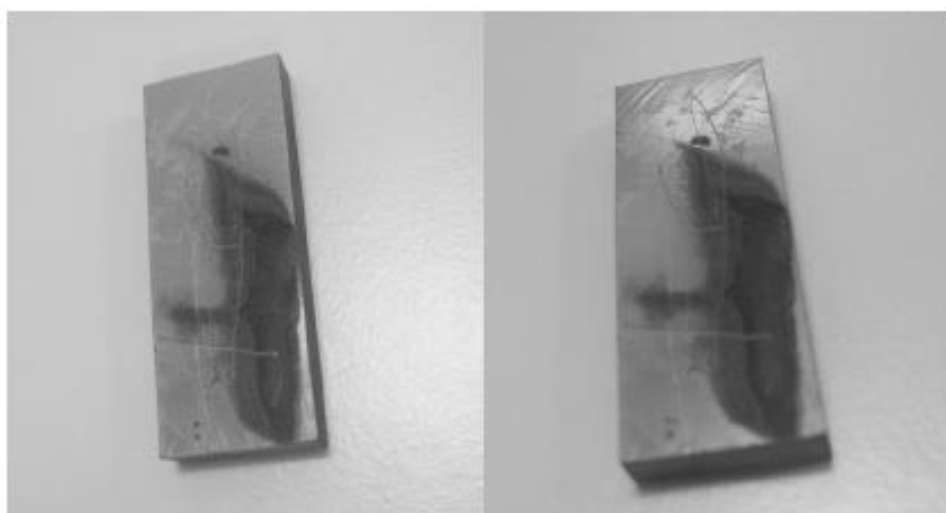


Fig. S14 Basic (left) and Acidic (right) environments with immersed [(3)₈₀-(2)₂₀] (top), surface etching of [(3)₈₀-(2)₂₀] (bottom) following exposure to NaOH for 3192 hours.

Table S1. Mass uptakes observed in 75.3 % RH studies

Material	Initial mass (M ₀)/g	Final mass (M _i)/g	H ₂ O absorption/%
<i>I</i> ₅₀ - <i>2</i> ₅₀	2.3344	2.3545	0.85
<i>I</i> ₆₀ - <i>2</i> ₄₀	1.9844	1.9996	0.76
<i>I</i> ₇₀ - <i>2</i> ₃₀	1.9211	1.9370	0.82
<i>I</i> ₈₀ - <i>2</i> ₂₀	1.1480	1.1572	0.80
<i>I</i> ₉₀ - <i>2</i> ₁₀	1.3742	1.3843	0.73
<i>3</i> ₅₀ - <i>I</i> ₅₀	2.1897	2.2040	0.65
<i>3</i> ₆₀ - <i>I</i> ₄₀	1.5209	1.5320	0.72
<i>3</i> ₇₀ - <i>I</i> ₃₀	1.9007	1.9163	0.81
<i>3</i> ₈₀ - <i>I</i> ₂₀	2.1262	2.1485	1.04
<i>3</i> ₉₀ - <i>I</i> ₁₀	1.7388	1.7583	1.11
<i>3</i> ₅₀ - <i>2</i> ₅₀	1.4718	1.4858	0.94
<i>3</i> ₆₀ - <i>2</i> ₄₀	1.9115	1.9301	0.96
<i>3</i> ₇₀ - <i>2</i> ₃₀	1.6132	1.6304	1.06
<i>3</i> ₈₀ - <i>2</i> ₂₀	1.7078	1.7273	1.13
<i>3</i> ₉₀ - <i>2</i> ₁₀	1.9839	2.0132	1.46

Table S2. Mass uptake observed in direct immersion studies

Material	Initial mass (M ₀) /g	Final mass (M _i) /g	H ₂ O absorption/ %
<i>1₅₀-2₅₀</i>	8.9461	9.0833	1.51
<i>1₆₀-2₄₀</i>	13.5747	13.8366	1.89
<i>1₇₀-2₃₀</i>	10.6314	10.827	1.81
<i>1₈₀-2₂₀</i>	12.9197	13.1641	1.86
<i>1₉₀-2₁₀</i>	7.5177	7.6385	1.58
<i>3₅₀-1₅₀</i>	17.2649	17.7285	2.61
<i>3₆₀-1₄₀</i>	17.3742	17.8680	2.76
<i>3₇₀-1₃₀</i>	12.7562	13.1457	2.96
<i>3₈₀-1₂₀</i>	15.4618	15.9268	2.92
<i>3₉₀-1₁₀</i>	13.8261	14.2588	3.03
<i>3₅₀-2₅₀</i>	13.5108	13.8650	2.55
<i>3₆₀-2₄₀</i>	17.2138	17.6260	2.34
<i>3₇₀-2₃₀</i>	15.4747	15.9267	2.84
<i>3₈₀-2₂₀</i>	11.8710	12.2167	2.83
<i>3₉₀-2₁₀</i>	15.6982	16.1960	3.07

Table S3. Thermogravimetric data for cured binary cyanate ester blends as determined by TGA (nitrogen, 10 K/minute)

Sample	Mass Loss at Temperature (°C)							Y _C (%)
	5 %	10 %	20 %	30 %	40 %	50 %	60 %	
<i>1</i>	413	423	428	435	458	538	575	1.83
<i>2</i>	417	422	430	452	530	571	588	1.89
<i>3</i>	423	434	522	595	620	635	650	1.76
<i>1</i>₅₀-<i>2</i>₅₀	414	422	427	436	484	549	576	2.03
<i>1</i>₆₀-<i>2</i>₄₀	411	419	421	422	429	470	551	1.54
<i>1</i>₇₀-<i>2</i>₃₀	416	425	427	436	470	542	570	1.45
<i>1</i>₈₀-<i>2</i>₂₀	413	425	430	438	489	552	579	1.22
<i>1</i>₉₀-<i>2</i>₁₀	410	424	428	435	458	530	552	1.76
<i>1</i>₃₀-<i>2</i>₅₀	416	425	441	522	572	595	608	1.38
<i>1</i>₆₀-<i>2</i>₄₀	419	426	460	552	592	610	622	1.59
<i>3</i>₇₀-<i>1</i>₃₀	420	429	498	573	604	621	635	1.65
<i>3</i>₈₀-<i>1</i>₂₀	420	431	498	578	609	625	640	1.33
<i>3</i>₉₀-<i>1</i>₁₀	419	434	515	585	603	619	633	1.67
<i>3</i>₅₀-<i>2</i>₅₀	420	430	484	558	592	608	621	1.41
<i>3</i>₆₀-<i>2</i>₄₀	420	432	489	560	594	612	624	1.75
<i>3</i>₇₀-<i>2</i>₃₀	408	423	429	487	555	587	604	1.47
<i>3</i>₈₀-<i>2</i>₂₀	420	434	513	574	603	619	633	1.58
<i>3</i>₉₀-<i>2</i>₁₀	418	433	508	566	597	614	628	1.34

Y_C = Char yield measured at 800 °C

Table S4. Mass uptakes observed in acid/base studies

Material	Initial mass (M ₀) /g		Final mass (M _i) /g		Mass change /%	
	H ₂ SO ₄	NaOH	H ₂ SO ₄	NaOH	H ₂ SO ₄	NaOH
<i>I</i>₅₀₋₂₅₀	2.086	2.208	2.1097	2.2348	+1.01	+1.01
<i>I</i>₆₀₋₂₄₀	1.672	1.449	1.6915	1.4670	+1.01	+1.01
<i>I</i>₇₀₋₂₃₀	2.289	2.363	2.1350	2.3897	+1.01	+1.01
<i>I</i>₈₀₋₂₂₀	1.892	1.768	1.9118	1.7904	+1.01	+1.02
<i>I</i>₉₀₋₂₁₀	0.641	0.481	0.6460	0.4865	+1.01	+1.01
<i>3</i>₅₀₋₁₅₀	1.776	1.750	1.7950	1.7700	+1.01	+1.01
<i>3</i>₆₀₋₁₄₀	1.816	2.370	1.8365	2.4016	+1.01	+1.01
<i>3</i>₇₀₋₁₃₀	2.217	1.458	2.2395	1.4773	+1.01	+1.01
<i>3</i>₈₀₋₁₂₀	1.909	2.427	1.9307	2.4620	+1.01	+1.01
<i>3</i>₉₀₋₁₁₀	1.720	1.889	1.7388	1.9242	+1.01	+1.02
<i>3</i>₅₀₋₂₅₀	1.254	1.327	1.2648	1.3380	+1.01	+1.01
<i>3</i>₆₀₋₂₄₀	1.335	0.970	1.3462	0.9810	+1.01	+1.01
<i>3</i>₇₀₋₂₃₀	1.930	2.052	1.946	2.0761	+1.01	+1.01
<i>3</i>₈₀₋₂₂₀	1.703	1.671	1.7265	1.6909	+1.01	+1.01
<i>3</i>₉₀₋₂₁₀	1.523	1.398	1.5408	1.4282	+1.01	+1.02